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LABORATORY PRECAUTIONS: No. 6.

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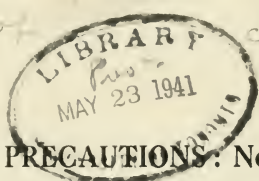
As is commonly the case, the neck of the bottle had slightly sloping sides which caused the rubber bung to creep upwards slowly, producing a gas leak. On pushing the rubber bung back again the slightly conical shape of the bottle neck deformed the rubber bung and caused the tips of the electrodes to touch while in the acid. A violent explosion resulted and the bottle was shattered.—J. R. B.

In such apparatus the rubber bung should be secured by string or wire.

Bleaching Powder.—A lever lid air-tight tin box containing about 2 lbs. of ordinary bleaching powder was stored in a cupboard in a dwelling house. After about six months, the owner going to the cupboard for a book kept there and seeing the box, thought he would open it and examine the contents. Before he had actually started to lever the lid it flew off with considerable explosive violence and a shower of finely divided bleaching powder was distributed over a large area, including the eyes and face of the unfortunate owner. Fortunately the eyesight was not destroyed, but the victim spent a most unhappy and painful period of suspense and a few days of dark room convalescence before being restored to normal. At the instant of the explosion the impression was of flame, and despite the immediate domestic cleaning up of the mess a later examination of the shelf confirmed this impression.

An explanation of the occurrence is not ventured, but it should be stated that a new tin was used though the actual condition of the bleaching powder with regard to moisture content was not known.—L. F.

Washing Reclaimed Silver Nitrate Crystals with Alcohol Leads to Explosion.—An explosion occurred in the chemical laboratory of the Pacific Biological Station, at Nanaimo, British Columbia, on 18th October, 1940, when reclaimed silver nitrate crystals were being washed with successive



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portions of ethyl alcohol. The technician conducting the process suffered silver nitrate burns on the face and eyes, lacerations about the head and hands, and the loss of two fingers from the left hand.

In this laboratory the silver chloride residues from routine Mohr titrations of sea water chlorinity are saved; the silver is reclaimed and silver nitrate prepared. Usually about 20 pounds of the chloride accumulates and the reclamation process is carried out on successive small lots of about two pounds each. Consequently, each step is carried out ten or twelve times.

The residues, containing adhering traces of sea water salts and silver chromate, are fused with sodium carbonate, and the molten metal separated from the slag by pouring into water. The metal is further purified by remelting and pouring into water a second time. The resulting mossy silver is treated in the cold with concentrated nitric acid which is heated to boiling as the rate of reaction decreases. The impure silver nitrate solution contains chromium, carried over from the original residues, iron and copper, from the fusion manipulations, and excess nitric acid. The liquor is evaporated under partial vacuum until crystals of silver nitrate separate, then cooled, the supernatant liquor decanted, and the crystals washed once with a small amount of distilled water. This process of crystal separation is successively repeated until the liquor volume has been reduced as much as practicable, when the residual silver ions are precipitated as chlorides and preserved until the next reclamation. The aqueous liquor contains practically all the excess nitric acid and nitrates of the less noble metals.

Prior to the explosion, the practice was to rinse the moist crystals, with adhering traces of metallic impurities and dilute nitric acid, two to four times with ethyl alcohol (denatured with 10 per cent. acetone). The alcohol was added to the crystals first obtained from the crystallisation process, the mass was stirred, and after settling the alcohol was decanted to the second lot, and so on. The silver was generally recovered by precipitation as chloride, although in several instances the solution was evaporated to dryness and the silver nitrate recovered. The alcohol washing was repeated until the desired appearance of the crystals was obtained. The several lots of alcohol-moist crystals were then combined and set in a warm place to dry.

At the time of the explosion a series of washings had been completed and the laboratory assistant was examining the last

lot of alcohol-moist crystals. He was holding a pyrex beaker containing about one-quarter pound of crystals in his left hand. When he touched them with a porcelain spatula the explosion occurred.

It was so rapid that only one sound wave appeared to be generated and consequently it may be classed as a detonation. The force was great enough to sever one of the assistant's fingers and break the top of the bench. Another assistant at a distance of four feet was knocked down, but the author at a distance of 12 feet did not feel the shock of the blast. Windows in the laboratory were pierced with high velocity particles, but were not shattered. After the explosion there was a strong odour of ethyl nitrate in the laboratory.

It is beyond doubt that silver fulminate was formed according to the reaction, $\text{AgNO}_3 + \text{HNO}_3 + \text{C}_2\text{H}_5\text{OH} \longrightarrow \text{AgONC} + ?$ and detonated. There is no possibility of fulminating silver (Ag_3N) having been formed as there was no ammonia in the laboratory at the time.

The alcohol washing technique was introduced to remove the adhering dissolved impurities from the crystals with a minimum waste of silver nitrate. Prior to using the process, an examination had been made in which a small amount of acid moist crystals had been rinsed with alcohol and evaporated to dryness. The possibility of violent reaction between nitric acid and alcohol had been recognised, but after repeated tests on a small scale it appeared that the amount of nitric acid present was not sufficient, in comparison to the amount of alcohol, to give any troublesome results. The process had been carried out successfully in the neighbourhood of 40 to 50 times without any indication of violence. The reactions leading to the formation of the fulminate were not recognised.

Silver nitrate is commonly used in all branches of chemistry and is frequently reclaimed and purified. It is also common practice to rinse and dry reagents in general with alcohol. This combination of circumstances presents an obvious opportunity for the re-occurrence of this mishap. Furthermore, during subsequent inquiry, it became evident that definite knowledge of the fulminate reactions, and the difference between fulminating silver and silver fulminate, is not general. Consequently it appears that the possibilities of such reactions should be stressed in undergraduate studies at the universities, particularly amongst analytical, inorganic, and physical chemistry students.

Suggested methods of purification.

In the reclamation of silver nitrate, the alcohol washing may be obviated in several ways, depending on the required state of the reclaimed salt.

1. If the acidity of the crude solution is the only objectionable characteristic, it may be neutralised with a sodium bi-carbonate solution until a faint precipitate of silver carbonate appears. The whole solution is then boiled to expel the free carbon dioxide, and more bi-carbonate added until a faint precipitate persists at the boiling point.

2. If it is required to reduce the concentration of the heavy metal nitrates, the crystals from the acid solution may be dissolved in water, made up to about 5 Normal, and the solution neutralised as above.

3. If it is necessary to remove the heavy metals, but alkali metals are not objectionable, the crude crystals may be rinsed with a saturated solution of sodium or potassium nitrate, as described under the alcohol technique.

4. Pure crystals may be obtained by recrystallising the alkaline nitrate-washed crystals from distilled water.

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